Advanced Nanofabrication Procedures and Applications

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Preface

Every book is a source of knowledge and this one is no exception. The idea that led to the conceptualization of this book was the fact that the world is advancing rapidly; which makes it crucial to document the progress in every field. I am aware that a lot of data is already available, yet, there is a lot more to learn. Hence, I accepted the responsibility of editing this book and contributing my knowledge to the community.

Nanofabrication is a broad field of study. Nanotechnology has witnessed a rapid expansion in the past few years, mainly owing to the speedy development in nanofabrication methods employed to manufacture nano-devices. Nanofabrication can be divided into two portions: methods using chemical combination and methods using nanolithography. This book contains various chapters and aims to offer the essential and current developments of nanolithography. It covers various aspects related to electron and ion beam, nanoimprint, interference, two-photon, UV and X-ray lithography. Most chapters analyze the lithographic procedures available for researchers and experts. This book covers the subject thoroughly and will be beneficial for its readers.

While editing this book, I had multiple visions for it. Then I finally narrowed down to make every chapter a sole standing text explaining a particular topic, so that they can be used independently. However, the umbrella subject sinews them into a common theme. This makes the book a unique platform of knowledge.

I would like to give the major credit of this book to the experts from every corner of the world, who took the time to share their expertise with us. Also, I owe the completion of this book to the never-ending support of my family, who supported me throughout the project.

Editor

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Focused Ion Beam Lithography

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1. Introduction

Optical lithography is the unrivalled mainstream patterning method that allows for cost-efficient, high-volume fabrication of micro- and nanoelectronic devices. Current optical photolithography allows for structures with a reproducible resolution below 32 nm. Nevertheless, alternative lithography methods coexist and excel in all cases where the requirement for a photomask is a disadvantage. Especially for low-volume fabrication of microdevices, the need for a photomask is inefficient and restricts a fast structuring, such as required for prototype device development and for the modification and repair of devices. The necessity of high-resolution masks with a price well above €10k is too cost intensive for the fabrication of single test devices. For this reason 'direct-write' approaches have emerged that are popular for several niche applications, such as mask repair and chip repair. Optical direct-write lithography and electron beam lithography are among the most prominent techniques of direct-write lithography. Less known, but highly versatile and powerful, is the ion beam lithography (IBL) method.

Optical direct-write lithography uses laser beam writers with a programmable spatial light modulator (SLM). With 500 mm^2/minute write speed and advanced 3D lithography capabilities, optical direct-write lithography is also suitable for commercial microchip fabrication. However, with a resolution of 0.6-µm minimum feature size of the photoresist pattern, optical direct-write lithography cannot be considered a nanopatterning method.

Electron beam lithography uses a focused electron beam to expose an electron beam resist. Gaussian beam tools operate with electron beams with a diameter below 1 nm so that true nanofabrication of structures is feasible. A resolution of 10 nm minimum feature size of the e-beam resist pattern has been successfully demonstrated with this method. However, special resists are required for e-beam lithography, that are compatible with the high energy of forward scattered, back-scattered and secondary electrons. A common resist for sub-50nm resolution is polymethylmetacrylate (PMMA) requiring an exposure dose above 0.2 $\mu C/\mu m^2$. For highest resolution (below 20 nm) inorganic resists such as hydrogen silsesquioxane (HSQ) or aluminium fluoride (AlF3) are used, which unfortunately require a high electron exposure dose. Hence, high-resolution electron beam lithography (EBL) is linked to long exposure times which, in combination with a single scanning beam, results in slow processing times. Therefore, this high-resolution method is only used for writing photomasks for optical projection lithography and for a limited number of high-end applications. A resolution to this dilemma may be the use of multi-beam electron tools, as are currently under development. Also electron projection lithography has been under

development but currently all development programmes for a commercial tool have been discontinued.
FIB lithography is similar to EBL, but provides more capabilities. Not only can FIB lithography (i) create a pattern in a resist layer just like EBL, but it is also capable of (ii) locally milling away atoms by physical sputtering with sub-10nm resolution (subtractive lithography), (iii) locally depositing material with sub-10nm resolution (additive lithography), (iv) local ion implantation for fabrication of an etching mask for subsequent pattern transfer and (v) direct material modification by ion-induced mixing.
The ion direct-write lithography combines the high resolution of electron beam lithography with the higher writing speed of optical laser writers. With so-called liquid metal ion sources focusing of the ion beam to a diameter down to 5 nm is feasible. Due to the higher mass of the ions the higher energy of the ion beam allows a faster exposure of resists and thus a higher processing speed. Currently, new ion sources have been developed and also ion projection systems and multi-beam systems are on the verge of commercial introduction, so that this "exotic" technique deserves more consideration for future nanofabrication.
FIB lithography is superior to EBL, as with focused ion beam (FIB) proximity, effects are negligible as no electron backscattering occurs. As a consequence, a higher resolution can be obtained with FIB as the pixel size is roughly equal to the beam spot size and no exposure occurs between pixels, hence allowing a short dwell time on each pixel. With the shorter ion range, weaker forward scattering and smaller lateral diffusion of secondary electrons, FIB lithography reaches a higher resolution than EBL with the same beam spot size. Overall, the higher resist sensitivity to ions increases the throughput in contrast to EBL.
A speciality of ion beam direct-write lithography is the possibility for resistless structuring. The application of a resist layer is not possible on non-planar samples, such as prestructured wafer surfaces or three-dimensional samples. If a resist layer can be applied, small structures are typically only feasible with ultrathin resist layers with a homogeneous thickness below 100 nm. The ion beam can also be used for direct-write implantation of direct-write milling of patterns in order to fabricate structures. The implantation of ions originating from the ion source itself can be used to fabricate locally doped hardmask layers that can be used for pattern generation in a subsequent selective etching process. This approach will be described in detail in section 4.3. The straightforward approach for pattern generation is the direct-write milling with a focused ion beam. The kinetic energy of accelerated ions may be used for physical sputtering of the substrate. With a focused Ga^+ ion beam of less than 5 nm diameter, structures with 30 nm features have been realized. This processing alternative will be described in detail in section 4.1. A sub-version of direct-write milling with an ion beam is the gas-assisted etching and the beam-induced deposition. The physical milling by the ion beam is complemented by a chemical reaction locally triggered by the energy of the ion beam. With gas-assisted etching, an etch gas is added that can react with the substrate to form a volatile etch product. With beam induced deposition a precursor gas is added that locally decomposes on those substrate areas scanned by the ion beam. From this ion beam-induced deposition, a solid material structure is formed. This is an 'additive' direct-write lithography technique.

2. Ion-solid interaction

The fundamental process of resist-based IBL is the ion-induced change of the resist. Typically, ion beam resists are used as negative resists experiencing a decrease of solubility of the ion exposed area due to ion-triggered reactions. Also with ion beam-induced etching and ion beam-induced deposition, a chemical reaction of surface species is the underlying mechanism of this structuring approach. For this reason, the ion-solid reaction shall be taken into closer examination.

Ion interaction with solid can be separated in elastic and inelastic collisions and in electronic interactions. Ion-atom as well as ion-electron collisions are typically treated as binary collisions. For the treatment of ion-atom collisions, a lower energy limit of 10 to 30 eV has to be considered. At lower energies, many body interactions are also a relevant mechanism, which is up to now widely neglected in literature due to its complexity (Eckstein, 1991).

Elastic collisions between ions and atoms of the substrate (or resist) are responsible for (i) beam broadening by scattering, (ii) amorphization of the target substrate, (iii) ion implantation into the target substrate, and (iv) sample physical sputtering. Both forward scattering and backward scattering lead to a broadening of the ion beam propagating in matter. As a practical consequence, this reduces the resolution when exposing a resist layer. Ions impinging into the substrate lead to the secondary effects of atomic mixing, which results in amorphization of crystalline samples, in the intermixing of resist and substrate at the interface and also implantation of the primary ions (often as an element) into the substrate. With photoresist, this may also lead to problems with later removal, as ion-implanted resists display a higher etch resistivity in plasma ashers. In the special case of sputtering, the substrate material is removed as a consequence of elastic collisions. The incident ions transfer their momentum to the target atoms within a collision cascade region. Atoms from the substrate surface may be ejected as a sputtered particle if it receives a kinetic energy that is sufficient to overcome the surface binding energy (SBE) of the target material. This effect is used for direct-write structuring by milling without any resist.

The ion beam may also be used to initiate chemical reactions. For this process, energy has to be converted from kinetic energy into other types of energy, such as bond dissociation energy. Such inelastic collisions involve an energy transfer either to electrons of the substrate ('electronic stopping') or an energy transfer to other nuclei or atoms of the substrate.

About two thirds of the dissipated energy is transformed into kinetic energy of so-called δ-electrons. Heavy ions dissipate their energy along their trajectories ionizing target atoms and producing free electrons. Around the ion's trajectory, secondary and tertiary ionization processes occur. Inelastic processes may lead to ionization of atoms involving also secondary electron emission. The secondary electrons are also subscribed a significant role in bond breaking mechanisms as a consequence of ion irradiation. Secondary electrons have energy between 1 and 50 eV corresponding to the energy range required to break molecular bonds (sigma and pi bonds). Other inelastic processes involve loss of kinetic energy by emission of photons including emission of x-rays, of Bremsstrahlung, or of Čerenkov radiation. Finally, heating, luminescence, shock wave or phonon excitation are other energy-loss mechanisms affecting not a single atom but rather an entire volume of the irradiated substrate.

Chemical reactions of the resist layer or of the substrate are induced by effects of inelastic collision of the primary ions. For chemical reactions of the resist layer, primarily the secondary electron-induced bond dissociation or the radical production is considered as a relevant mechanism. The low-energy secondary electrons (generated by ion-matter interaction) can expose a resist layer for lithography analogous to the secondary electron induced reactions used in EBL. Hence, electron beam resists can also be used as FIB lithography resists.

FIB lithography has the advantage of (i) a higher resolution due to the absence of proximity effects and (ii) a higher resist sensitivity. As no electron backscattering exists, the pixel size with FIB lithography is equal to the ion beam spot size and thus can be much higher than with EBL. As a primary ion can release up to 200 secondary electrons (Dietz & Sheffield, 1975), while a primary electron can release less than 2 secondary electrons (Hoyle, 1994) the exposure speed with ion lithography can be up to a factor of 100. On the other hand, FIB lithography resists suffer from a restricted exposure depth in the resist and from contamination of the resist by source ions. To circumvent larger structures resulting from the restricted exposure depth, a thin resist layer can be used, but this makes subsequent etching processes or lift-off processes more difficult. The contamination of the resist is especially problematic, if organic resists are removed by plasma ashing and the inorganic contaminations remain on the surface.

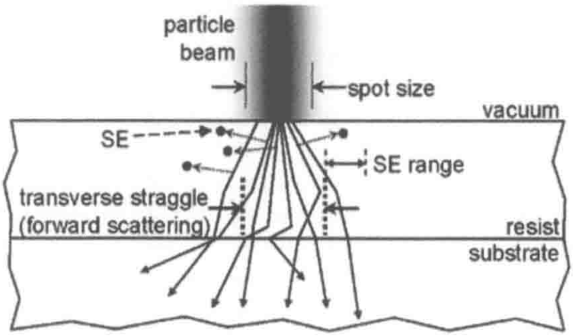

Fig. 1. Factors limiting resolution of IBL. A focused ion beam irradiates a resist layer on a substrate. The three factors limiting resolution are (i) spot size of the beam (ii) ion scattering and (iii) secondary electron emission.
Reprinted with permission from Winston D. et al., 2009. Scanning-helium-ion-beam lithography with hydrogen silsesquioxane resist. JVST B 27(6), 2702. Copyright 2009, American Vacuum Society.

Ion beam lithography has repeatedly been successfully used for exposing resist layers.
Structural modification of the resist, including chain scission, cross-linking, double-bond formation, molecular emission, changes in molecular weight distribution, and so forth are due to ion irradiation of polymers (Calcagno et al., 1992). The degradation of PMMA by proton beam irradiations for resist applications has been analyzed by Choi et al. (Choi et al., 1988). Even though the energies of the radiation sources varied considerably (up to 900 keV for H3+), they observed a 1-to-1 correspondence of loss of ester groups and generation of double bonds in the polymer chains for all radiation types.
Horiuchi et al. (Horiuchi et al., 1988) have achieved 200 nm line width in PMMA using a He+ ion beam. Using a Ga+ beam Kubena et al. (Kubena et al., 1989) could even demonstrate sub-20 nm line width in PMMA. The higher energy transmission by the ions allows for faster exposure of resists by ion beams so that also resists requiring prohibitively high electron doses with EBL can be used in IBL. Therefore, inorganic high-resolution resists such as hydrogen sesquioxane (HSQ) and aluminium fluoride can also be used. Hydrogen silsesquioxane (HSQ) is a negative-tone resist that cross-links via Si–H bond scission (Namatsu et al., 1998). The energy of a Si–H bond is roughly 3 eV and can be broken by secondary electron energy. Van Kan et al. (van Kan et al., 2006) have successfully demonstrated 22 nm line width in HSQ using a 2 MeV H_2^+ beam.